Nanostructured Electrodes

DOI: 10.1002/anie.200802988

Synthesis and Electrode Performance of Nanostructured V_2O_5 by Using a Carbon Tube-in-Tube as a Nanoreactor and an Efficient Mixed-Conducting Network**

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For the past decade, nanostructuring has been becoming one of the most powerful means to improve electrochemical performance of electrode materials in terms of both energy and power densities in rechargeable lithium-based energy-storage devices which have a wide range of promising applications in portable electronic devices and in powering electric vehicles.[1–6] Nanostructuring is very helpful in improving the electroactivity of electrode materials (e.g. Li storage in nanostructured TiO_2[6c,7] and MnO_2[8] with rutile structure), in improving the cycle life of electrode materials (e.g. Li storage in nanostructured Ni-Sn[3a] and Si[9]), and especially in improving discharge/charge rate capability of electrode materials.[1,3a,6e,f,10] Very recently, an optimized nanostructure design of electrode materials for high-power and high-energy lithium-ion batteries was proposed.[6e,f] The major characteristic tool is the introduction of hierarchical mixed-conducting networks (that is, networks that can conduct both ions and electrons). These networks involve the combination of both the nano- and microscale materials through which the effective diffusion length for both electrons and ions is reduced to only several nanometers. The concept was realized by the synthesis of mesoporous TiO_2:RuO_2 and C-$LiFePO_4$:RuO_2 nanocomposite electrodes which show high rate capabilities when used as the anode and cathode materials for lithium batteries. The key to its success is both the preparation of mesopores which render the electrolyte diffusion into the bulk of the electrode material facile and hence provide fast transport channels for the conductive ions (e.g., solvated Li^+ ions), and the coating of pore channels by a good electronic conductor—the oxide RuO_2—that enables fast electronic transport pathway. However, RuO_2 is an expensive material, a cost-effective alternate is desired for such nanostructure. Carbon is one of the best choices because of its high electronic conductivity, good lithium permeation, and electrochemical stability. The carbon-coating technique is widely applied in a variety of electrode materials.[9a,10g,11–13] However, the synthesis of such nanocomposites is complicated and the thickness of carbon shell needs to be controlled to a few nanometers and the porosity required for Li migration through this layer must be obtained.

Herein, we propose the use of a nanoarchitectured electrode composed of an efficient mixed-conducting network (Figure 1 a), in which carbon tube-in-tube (CTIT) serves as "electronic wire" which provides the electrons to the active materials and the specifically designed tube diameter of the CTIT allows for easy electrolyte access. Such a nanostructure provides both an electronic pathway and a lithium-ion pathway which are essential for a high rate rechargeable lithium battery. We also show that CTIT can be employed as a nanoreactor for the synthesis nanomaterials, by exploiting its multiple channels and the possibility of confining reagents within them. This concept was realized by the synthesis of V_2O_5/CTIT nanocomposites, which show significantly improved Li insertion/extraction kinetics and a very high

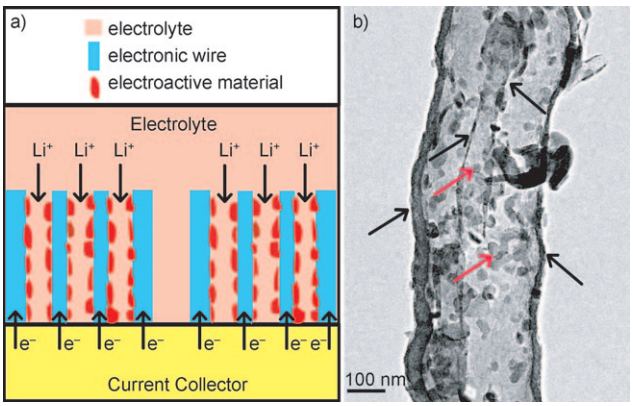

Figure 1. a) Schematic representation of the desired design based on an efficient mixed-conducting network. b) Typical TEM image of the V_2O_5/CTIT nanocomposites showing that most of the V_2O_5 nanoparticles are encapsulated within CTIT. The V_2O_5 nanoparticles indicated by red arrows and CTIT indicated by black arrows.

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[**] The authors thank G. Götz and A. Schulz for their technical support; Dr. R. Merkle for TG measurement; Drs. J. Jamnik, R. Dominko, and Y.-G. Guo for helpful discussions. The authors are indebted to the Max Planck Society and acknowledge support in the framework of the ENERCHEM project.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802988.

rate performance when used as a cathode material for lithium batteries.

Well-organized CTIT was successfully synthesized by a wet-chemical reorganization of the carbonaceous impurities in freshly prepared carbon nanotubes.[14] The morphology and microstructure of freshly prepared carbon nanotubes and CTIT are shown in Figure S1 of the Supporting Information. The freshly prepared carbon nanotubes displayed the fish-boned microstructure combined with poorly graphitic carbon deposits (Figure S1b in the Supporting Information). After oxidation and reintegration treatment,[14] the carbon deposit was exfoliated and a new tube with a thickness ranging from 10 to 20 nm formed along the long axis of the carbon nanotube as observed in the TEM images (Figures S1 c,d in the Supporting Information display the bi-tubular coaxial microstructure).

The fabrication mechanism of CTIT has been discussed elsewhere.[14] It suggests that the graphene sheets exfoliated from the carbon deposits and impurities self-assemble along the carbon nanotube which acts as a template. Owing to the facile wet-chemical synthetic route, CTIT can be produced at low cost and on a large scale, which are prerequisites of large-scale applications. The multiple channels and surfaces of the CTIT are readily accessible for guest materials.

V_2O_5, whose various nanostructures (e.g. nanotubes, nanorods, nanofibers, nanowires, nanobelts, and mesoporous structures) have been extensively investigated as a cathode material in lithium batteries,[5,10c,h,13,15–26] was selected in this case to demonstrate the usefulness of the nanostructure design. By simply adding an aqueous solution of vanadate oxalate into the as-synthesized CTIT and subsequent heat treatment in air at 400 °C for 2 h, a uniform coating of vanadium oxide nanoparticles was achieved. This coating can be clearly observed within the cylindrical and interval spaces of the CTIT and on the multiple surfaces by TEM (Figure 1 b and Figure S2 a,b in the Supporting Information). (A few V_2O_5 nanoparticles were also formed on the external surface of CTIT.) To confirm that most of the V_2O_5 nanoparticles were encapsulated within the CTIT, we carried out TEM studies with varying tilt angle (see Figure S3 in the Supporting Information). These results show that most of the smaller nanoparticles are inside the CTIT, this is a result of the capillary force of the nanotubes. However, a few big particles were also found outside of CTIT. Clearly the driving force behind filling the CTIT with the vanadium precursor solution is surface interactions. Once the vanadium precursor is loaded into the CTIT, it can be converted into vanadium oxide nanoparticles by thermal treatment, a conversion that is favored by confinement in the tube space. The particle size is mostly around 30 nm. According to thermogravimetric (TG) measurements (not shown), the CTIT content is around 15 wt % in the nanocomposites. (Note that because only 70 % CTIT formed in synthetic process, V_2O_5 nanoparticles were also observed in the residual carbon nanotubes, see Figure S2 c in the Supporting Information.) The results obtained indeed show that CTIT can be used as a nanoreactor to synthesize nanostructured inorganic compounds.

Figure 2 depicts the X-ray diffraction (XRD) and Raman spectrum of the nanocomposite. The XRD pattern indicates

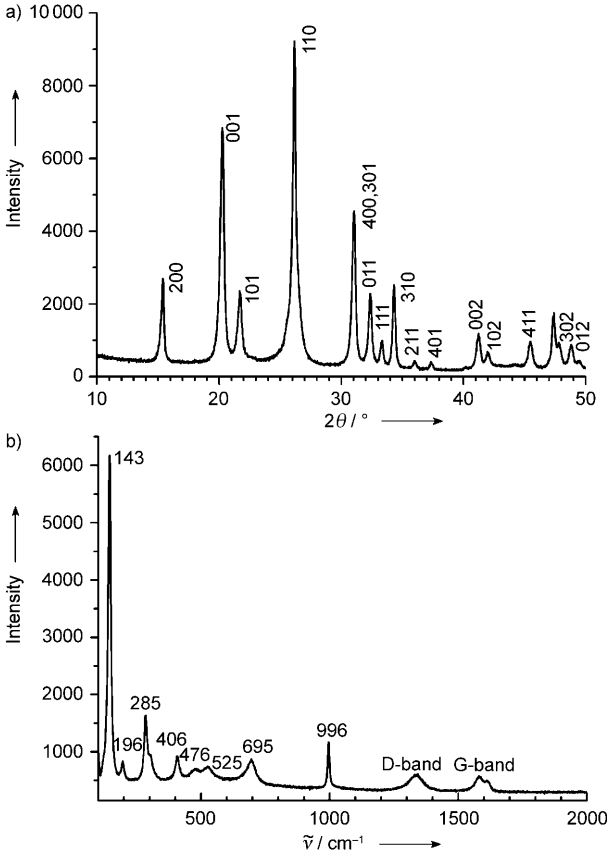

Figure 2. a) XRD pattern and b) Raman spectrum of the V_2O_5/CTIT nanocomposites.

the presence of crystalline V_2O_5 and can be indexed according to the orthogonal symmetry of V_2O_5 (space group: *Pmmn* (No. 59), $a = 1.1516$, $b = 0.3565$, $c = 0.4372$ nm; JCPDS card No. 41-1426).[5] It can be also observed that the Bragg peaks are somewhat broadened, suggesting the presence of small crystalline particles. According to LeBail's method, crystallite dimensions of about 30 nm can be deduced for the V_2O_5 nanoparticles, which is in good agreement with the TEM results. Raman spectrum indicates the coexistence of two phases, namely V_2O_5 and carbon, in the resulting nanocomposites.[25]

As there is close electrical contact between the two phases at the nanoscale level at many points along the wall of the CTIT (see HRTEM images in Figure S4 of the Supporting Information) and as the material is easily accessible to the electrolyte, the kinetics of Li insertion/extraction and the Li storage performance can be expected to be improved in this V_2O_5/CTIT nanocomposite over those of conventional materials. Cyclic voltammetry was used to investigate the Li insertion/extraction behavior. For comparison, commercially available micrometer-sized V_2O_5 was also tested (see Figure S5,6 in the Supporting Information). Figure 3 shows cyclic voltammograms (CVs) of both the V_2O_5/CTIT nanocomposite electrodes and of V_2O_5 microparticle electrodes. The two pairs of redox peaks at around 3.4 V and 3.2 V were observed for both electrodes, and are typically ascribed to the

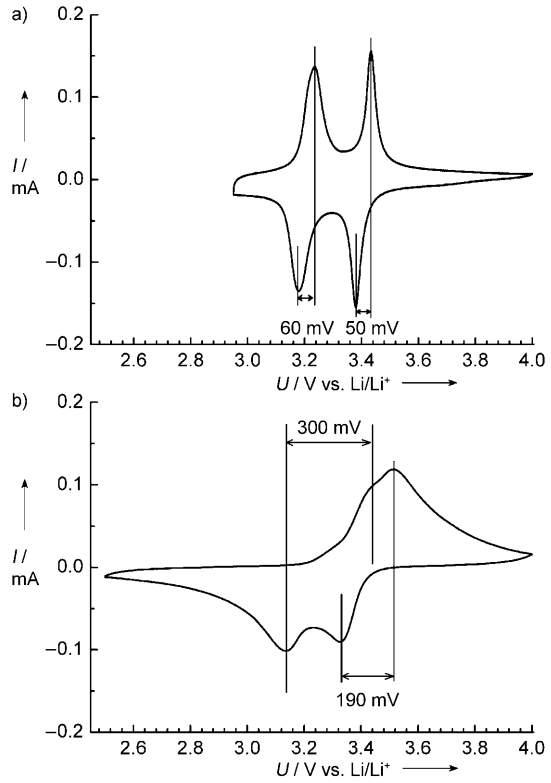

Figure 3. Cyclic voltammograms of a) the V_2O_5/CTIT nanocomposite and b) V_2O_5 microparticles at a scan rate of 0.1 mV s^{-1}.

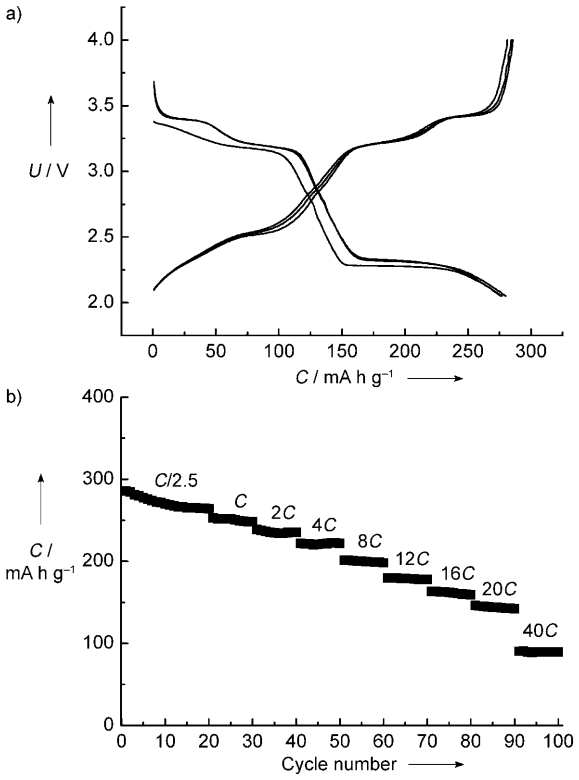

Figure 4. a) The first three cycles of galvanostatic discharge (Li insertion, voltage decreases)/charge (Li extraction, voltage increases) curves of the V_2O_5/CTIT nanocomposite electrode cycled at a current density of *C*/2.5 between voltage limits of 2.0–4.0 V in 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate solution. b) Cycling and discharging/charging rate performance of the V_2O_5/CTIT nanocomposite electrode.

reversible reaction of lithium with crystalline V_2O_5 in a two-step electrochemical processes [Eq. (1) and (2)].[5,13]

$$V_2O_5 + 0.5\,Li^+ + 0.5\,e^- \rightleftharpoons Li_{0.5}V_2O_5 \quad (1)$$

$$Li_{0.5}V_2O_5 + 0.5\,Li^+ + 0.5\,e^- \rightleftharpoons LiV_2O_5 \quad (2)$$

In the case of the V_2O_5/CTIT nanocomposite, the differences between the cathodic and anodic peaks for the redox reactions at around 3.4 and 3.2 V (so-called polarization) are 50 mV and 60 mV, respectively, which are much lower than those of microscale V_2O_5 (190 and 300 mV) at the same experimental condition. In addition, the voltages of anodic peaks at around 3.4 and 3.2 V for the V_2O_5/CTIT nanocomposite are about 50 mV higher than those of microscale V_2O_5. These results clearly show that the kinetics of lithium insertion/extraction in the V_2O_5/CTIT nanocomposite are greatly improved by the close electrical contact between the nanoscale V_2O_5 and CTIT.

Figure 4a shows the first three cycles of galvanostatic discharge (Li insertion) and charge (Li extraction) curves of the V_2O_5/CTIT nanocomposite electrodes. Three plateaus at 3.4, 3.2, and 2.3 V can be observed in the discharge curves. The first two plateaus correspond to the reactions in Equations (1) and (2), which are in good agreement with the CV curves. The reversible capacity related to these processes is around 130 mA h g^{-1}, which is close to the theoretical capacity of 147 mA h g^{-1} for one lithium per formula unit (V_2O_5). The capacity is also significantly higher than for microscale V_2O_5.[26] The third plateau at 2.3 V can be ascribed to a further lithium insertion into LiV_2O_5, which is also highly reversible [Eq. (3)],[5,13]

$$LiV_2O_5 + 1\,Li^+ + 1\,e^- \leftrightarrow Li_2V_2O_5 \quad (3)$$

A total reversible capacity of about 280 mA h g^{-1} in the voltage range of 2.0–4.0 V was obtained for the V_2O_5/CTIT nanocomposite at a rate of *C*/2.5. Furthermore, in the charging process, nearly the same amount of lithium can be removed, corresponding to a coulombic efficiency of above 99%. In addition, it was found that on cycling the capacity retention is good. Another property of this V_2O_5/CTIT nanocomposite is the high rate capability. Results are shown in Figure 4b in which rates of up to 40 *C* have been employed. The cell was first cycled at *C*/2.5 and, after 20 cycles, the rate was increased in stages to 40 *C*. A specific charge capacity of around 265 mA h g^{-1} with a coulombic efficiency of nearly 100% was obtained at a rate of *C*/2.5 (58.8 mA g^{-1}) after 20 cycles; this value is lowered to 250 mA h g^{-1} at 1 *C* (147 mA g^{-1}), 223 mA h g^{-1} at 4 *C* (588 mA g^{-1}), 200 mA h g^{-1} at 8 *C* (1.176 A g^{-1}), 180 mA h g^{-1} at 12 *C* (1.764 A g^{-1}), 160 mA h g^{-1} at 16 *C* (2.352 A g^{-1}), 140 mA h g^{-1} at 20 *C* (2.940 A g^{-1}), and finally, 90 mA h g^{-1} at 40 *C* (5.880 A g^{-1}). This rate capability is higher than those of carbon-coated V_2O_5 and other V_2O_5-based electrodes.[13,15,17] The experi-

mental results obtained show that the mixed-conducting nanostructure favorably reduces the diffusion length for lithium ions and enables the high rate performance of lithium-based batteries.

In summary, an optimized nanostructured electrode design has been proposed. This nanoarchitecture is realized by the synthesis of the V_2O_5/CTIT nanocomposites which show a significantly improved lithium-storage performance in terms of the kinetics for Li insertion/extraction, highly reversible lithium-storage capacity, good cycling performance, and high rate capability, making it a promising candidate as a cathode material in lithium-ion batteries. This design could also be extended to other cathode and anode electrode active materials that find application in energy-storage devices: for example, iron- and manganese-based phosphate cathodes.[10–12]

Experimental Section

Preparation of V_2O_5/CTIT nanocomposites:Details of the synthesis of the CTIT has been reported elsewhere.[14] The CTIT supported V_2O_5 nanomaterial was prepared by the incipient wetness impregnation method from ammonium metavanadate (NH_4VO_3) dissolved in oxalic acid solution. The concentration of NH_4VO_3 was 2.1 mol L^{-1} and the molar ratio of NH_4VO_3 to $C_2O_4H_2$ was 1:2. The solution was introduced into the CTIT lumen by a wet chemistry using the capillary forces of nanotubes. After impregnation, the sample was dried in air at 80 °C overnight and then calcined at 400 °C for 2 h. The loading amount of V_2O_5 was approximately 80 wt %.

Structural Characterizations: A Philips TEM CM 200 Lab6 and Philips TEM/STEM CM 200 FEG transmission electron microscope were used to study the morphology and microstructure of the V_2O_5/CTIT nanocomposites. The acceleration voltage is set to 200 kV. X-ray diffraction (XRD) patterns were recorded on a Philips instrument using $Cu_{K\alpha}$ radiation. Micro-Raman spectra were recorded on a Jobin Yvon LabRam spectrometer using a 632.8 nm excitation laser line. Thermogravimetric analysis was carried out using a NETZSCH STA 449C (NETZSCH-Geraetebau GmbH Thermal Analysis) at a heating rate of 10 K min^{-1} under a mixture of N_2 (5 mL)/O_2 (20 mL).

Electrochemical Characterizations: Electrochemical experiments were performed using two-electrode Swagelok-type cells. For preparing working electrodes, a mixture of V_2O_5/CTIT nanocomposites or pure V_2O_5, carbon black, and polyvinylidene fluoride (PVDF) at a weight ratio of 80:10:10, was pasted on pure Al foil (99.6%, Goodfellow). Glass fiber (GF/D) from Whatman was used as a separator. The electrolyte consists of a solution of 1M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, in volume) obtained from Ube Industries Ltd. Pure lithium foil (Aldrich) was used as counter electrode. The cells were assembled in an argon-filled glove box. The discharge and charge measurements were carried out at different current densities (herein 1*C* refers to 1 lithium per formula unit (V_2O_5) discharged/charged in 1 h) in the voltage range of 2.0–4.0 V on an Arbin MSTAT battery test system. The specific capacity of the V_2O_5/CTIT nanocomposites was calculated by using the total mass of V_2O_5+CTIT. Cyclic voltammogram measurements were performed on VoltaLab 80 electrochemical workstation at a scan rate of 0.1 mV s^{-1}.

Received: June 22, 2008
Revised: September 30, 2008
Published online: November 28, 2008

Keywords: electrochemistry · lithium-ion batteries · nanoreactors · nanostructures · nanotubes · V_2O_5

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